

Probing the local structure: macromolecular combs in external fields

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Abstract

Recent experimental methods allow to monitor the response of macromolecules to locally applied fields, complementing usual, mesoscopic techniques. Based on the Rouse-model and its extension to generalized Gaussian structures (GGs), we follow here the stretching of comb macromolecules under local fields. This leads to a wealth of informations about the structure: Namely, given the inhomogeneous architecture of combs, the dynamics and amount of stretching depend strongly on the position of the monomer on which the external fields act. We discuss both the theoretical and the experimental implications of our findings, given that micromanipulations can be supplemented by fluorescence measurements, which are very sensitive to changes in the intramolecular distances.

I. INTRODUCTION

Due to numerous technological applications, understanding the structural and dynamical properties of branched polymers and of polymer networks is of much interest.^{1,2} Here a very challenging question is to determine how the topology affects the dynamical properties.¹⁻⁴ Apart from the classical, bulk determination of the relaxation moduli, nowadays one can also act microscopically on dilute polymers in solution; for instance one can locally apply electrical fields on charged polymers (polyelectrolytes, polyampholytes), magnetic fields on magnetizable beads, or optical tweezers on dielectric spheres attached to the macromolecules.⁵⁻⁸ Now, the extension of the macromolecule under such external fields depends, evidently, on the underlying topology and, especially, on the site on which the field acts. In previous works we have shown that this site dependence gets to be more pronounced, when the structure is more ramified; thus dendrimers^{4,9} show larger site differences than linear chains and regular fractals.¹⁰⁻¹³

In this paper we study the stretching of comb-polymers¹⁴⁻¹⁸ whose backbones are linear chains, and especially the stretching of ring-backbones out of which sprout linear chains. As stressed, we choose these systems in order to study in detail the differences encountered when applying local fields to different constituents of rather heterogeneous macromolecules; furthermore, we know that dynamical features of comb-like structures can differ vastly, in the asymptotic limit, from the behavior encountered in objects with regular topologies.¹⁹⁻²¹

As we proceed to show, modern measurements which allow to pinpoint the external fields on local parts of large macromolecules lead, based on their dynamical stretching, to a quite detailed picture of the underlying connections inside the structure. Such changes in the distances inside the macromolecule can be monitored directly, say by attaching a donor and an acceptor chromophore to different parts of the structure and by following the corresponding excitation transfer;²²⁻²⁶ due to the high sensitivity of the transfer on the mutual distance, the method is very accurate, being of much use in polymer sciences.²⁴⁻³³

In order to discuss the general situation and to stress the main features we restrict

ourselves to the basic ideas of the Rouse-model,^{34–36} as implemented in the generalized Gaussian-structures (GGS) scheme.^{10,37} Now using the GGS simplifies much the calculations, given that in this scheme the effects of the hydrodynamic interactions and of possible memory effects are neglected. Also neglected are local geometrical aspects, such as the excluded volume and the stiffness of the chains. Given, however, that our intention here is to show how much additional information can be obtained from micromanipulations (as contrasted to the usual bulk experiments) we prefer to work in the GGS picture, while being well-aware of the fact that a quantitative comparison to experiments must take additional features into account.

We recall that GGS consist of beads connected to each other by springs, beads which feel the influence of the embedding medium through its viscosity. The main theoretical advantage of centering on GGS is that they allow to show the close interconnection between topology and dynamics. Namely, as stated before in the GGS scheme many macroscopical observables of polymer physics and of physical chemistry are simply related to the *eigenvalues*^{1,2,4,10,35} of the connectivity matrices of the GGS. However, these observables do not depend on the corresponding eigenvectors. The *local* probing of such structures, on the other hand involves directly the *eigenvectors*,^{4,9,10} fact which leads to a much wider class of possible dynamical behaviors. In the case of comb-molecules, as we will show, letting the force act closely to the tips or closely to the backbone of the structure leads to markedly different responses. Possible ways to monitor such responses are the tracking of the motion through fluorescent probes, as well as nuclear-resonance and electronic energy transfer, the later methods being very sensitive to changes in the relative distances inside the macromolecule.^{22–33}

The paper is structured as follows: In the next Section we discuss the GGS-model and its implications for the dynamics. We recall in particular how several basic, experimentally readily accessible quantities are related to the properties of the connectivity matrix; in this Section we also show how the positions on which the local forces act influence the stretching of the macromolecules involved. Section III is devoted to the calculation of the stretching of comb-molecules in external fields; in this Section we also discuss our numerical findings

related to the position-dependent dynamics and give approximate analytical expressions for the response functions to external fields. We focus in particular on the time-regime intermediate between very small times (at which only small parts of the molecule are in motion) and very long times (where the whole molecule moves); such intermediate times are most revealing for the comb-like structures under investigation. We conclude our work in Sec. IV with a discussion of results and with indications about their implications for further theoretical and experimental studies.

II. GENERALIZED GAUSSIAN STRUCTURES

In this section we consider the dynamics of Gaussian generalized structures (GGS), whose simplest representation is the Rouse chain.³⁴ We follow the usual development of the theory,^{10–12, 35–43} while paying particular attention to the extension of the GGS in external fields. As indicated above, recent optical and mechanical developments allow one to micromanipulate such GGS in solution.

We model the GGS as a complex consisting of N beads, which are connected to each other by harmonic springs. As usual, we assume that each monomer experiences the friction coefficient ζ and that all beads move under the influence of random forces, included here via the velocities $\mathbf{w}(t)$. Taking as usual the distribution of the $\mathbf{w}(t)$ to be Gaussian and zero-centered, one obtains the following linearized Langevin equation for the dynamics of the beads,^{35–37, 40, 42} where one denotes the coordinate of the i -th bead by \mathbf{R}_i and the external force acting on it by \mathbf{F}_i :

$$\frac{\partial \mathbf{R}_i(t)}{\partial t} + \sigma \sum_{j=1}^N A_{ij} \mathbf{R}_j(t) = \mathbf{w}_i(t) + \frac{\mathbf{F}_i(t)}{\zeta}. \quad (1)$$

Note that $\mathbf{A} = (A_{ij})$ in Eq. (1) is the connectivity matrix.^{37, 40, 41} The matrix \mathbf{A} can be constructed by initially setting all elements to zero and accounting for each bond between the monomers i and j by increasing the diagonal elements A_{ii} and A_{jj} by +1 and the non-diagonal elements A_{ij} and A_{ji} by -1. Note that in this way \mathbf{A} is a symmetric constant

matrix. Furthermore $\det(\mathbf{A}) = 0$, as is evident by construction, and which implies that (at least) one eigenvalue vanishes. More compactly, Eq. (1) reads:

$$\frac{\partial \mathbf{R}(t)}{\partial t} + \sigma \mathbf{A} \mathbf{R}(t) = \mathbf{w}(t) + \frac{\mathbf{F}(t)}{\zeta} \quad (2)$$

with $\mathbf{R} \equiv (\mathbf{R}_1, \mathbf{R}_2 \cdots, \mathbf{R}_n)^T$, $\mathbf{w} \equiv (\mathbf{w}_1, \mathbf{w}_2 \cdots, \mathbf{w}_N)^T$ and $\mathbf{F} \equiv (\mathbf{F}_1, \mathbf{F}_2, \cdots, \mathbf{F}_N)^T$, where T denotes the transposed vector.

The solution of Eq. (2) can be written as^{4,9}

$$\mathbf{R}(t) = \int_{-\infty}^t dt' \exp[-\sigma(t-t')\mathbf{A}] \left[\mathbf{w}(t') + \frac{\mathbf{F}(t')}{\zeta} \right]. \quad (3)$$

One can now diagonalize the connectivity matrix and has formally

$$\mathbf{A} = \mathbf{Q} \mathbf{\Lambda} \mathbf{Q}^{-1}, \quad (4)$$

where $\mathbf{\Lambda}$ is a diagonal matrix built from the eigenvalues of \mathbf{A} and \mathbf{Q} is the matrix of the corresponding eigenvectors. Inserting Eq. (4) into Eq. (3) leads to the mean displacement:

$$\langle \mathbf{R}(t) \rangle = \int_{-\infty}^t dt' \mathbf{Q} \exp[-\sigma(t-t')\mathbf{\Lambda}] \mathbf{Q}^{-1} \frac{\mathbf{F}(t')}{\zeta}. \quad (5)$$

In Eq. (5) the average goes over the random velocities \mathbf{w} . We now focus on the special case in which a constant external force is switched on at $t = 0$ and acts on the m -th bead only, i.e. $\mathbf{F}_i(t) = \mathbf{F}_0 \delta_{i,m} \sigma(t)$. The evaluation of $\langle Y_m(t) \rangle$, the mean displacement of the m -th bead between times 0 and t is most readily performed by choosing the y -coordinate in the direction of the force. We obtain then from Eq. (5):

$$\begin{aligned} \langle Y_m(t) \rangle &= \frac{F_0}{\zeta} \sum_{i=1}^N \int_0^t dt' Q_{mi} \exp[-\sigma \lambda_i(t-t')] Q_{im}^{-1} \\ &= \frac{F_0 t}{N \zeta} + \frac{F_0}{\sigma \zeta} \sum_{i=2}^N Q_{mi} \frac{1 - \exp(-\sigma \lambda_i t)}{\lambda_i} Q_{im}^{-1}, \end{aligned} \quad (6)$$

where we set $(\mathbf{Q}^{-1})_{im} \equiv Q_{im}^{-1}$, noticed that these quantities are independent of t and hence performed the integration over t in straightforward manner. Note that on the rhs of Eq. (6) the motion of the center of mass (CM) has separated automatically from the rest.^{4,10} The CM is characterized by the vanishing eigenvalue $\lambda_1 = 0$.

Eq. (6) is the fundamental quantity for our further studies; one may note that it depends both on the eigenvalues and on the eigenvectors of the connectivity matrix \mathbf{A} . Before proceeding to analyse Eq. (6) we recall that averaging it also over all positions m leads to an extremely simple form, namely to¹⁰

$$\langle\langle Y(t) \rangle\rangle = \frac{F_0 t}{N\zeta} + \frac{F_0}{\sigma N\zeta} \sum_{i=2}^N \frac{1 - \exp(-\sigma\lambda_i t)}{\lambda_i}. \quad (7)$$

In Eq. (7) one should remark that only the eigenvalues of the matrix \mathbf{A} , but not the eigenvectors are involved. Eq. (7) is, in fact, related to the dynamical response function (relaxation modulus) $G(t)$ of the structure

$$G(t) = \frac{1}{N} \sum_{i=1}^N e^{-\sigma\lambda_i t} \quad (8)$$

through:

$$\langle\langle Y(t) \rangle\rangle = \frac{F_0}{\zeta} \int_0^t G(\tilde{t}) d\tilde{t}. \quad (9)$$

This relation shows that $G(t)$ plays the role of a fundamental dynamical expression. In fact, $G(t)$ is also connected to other basic observables, such as $G'(\omega)$, the storage modulus and $G''(\omega)$, the loss modulus.^{35,40,43,44} Now $G'(\omega)$ and $G''(\omega)$ are proportional to the real and the imaginary part of the Fourier-transformed $i\omega G(2t)$; one has namely

$$G'(\omega) = A \sum_{i=2}^N \frac{\omega^2}{\omega^2 + (2\sigma\lambda_i)^2} \quad (10)$$

for the storage modulus and

$$G''(\omega) = A \sum_{i=2}^N \frac{2\sigma\omega\lambda_i}{\omega^2 + (2\sigma\lambda_i)^2} \quad (11)$$

for the loss modulus, where in Eqs. (10) and (11) for a given sample and at a fixed temperature T the prefactor A is a constant.

In the next section we will discuss the stretching of comb-rings (a special family of comb-like molecules) in the framework of the GGS dynamics discussed here. The stretching $\delta Y(t)$ is given by subtracting from Eq. (6) the motion of the CM, *i.e.* :

$$\begin{aligned}
\langle \delta Y_m(t) \rangle &= \langle Y_m(t) \rangle - \frac{F_0 t}{N \zeta} \\
&= \frac{F_0}{\sigma \zeta} \sum_{i=2}^N Q_{mi} \frac{1 - \exp(-\sigma \lambda_i t)}{\lambda_i} Q_{im}^{-1}.
\end{aligned} \tag{12}$$

III. NUMERICAL EVALUATION OF THE STRETCHING OF COMB-RINGS

In this Section we evaluate the stretching $\langle \delta Y_m(t) \rangle$ of comb-rings structures under external fields. For this we start from comb molecules, consisting of a backbone made up of M_1 monomers, to which we attach linear chains of $M_2 - 1$ monomers each. For simplicity, we apply periodic boundary condition *to the backbone*, or, equivalently, we close the backbone into a ring. The situation is depicted in Fig. 1 where we have $M_1 = 9$ and $M_2 = 4$. As a further simplification we set $M_1 = M_2 = M$ and choose M to be 50, by which we have $N = 2500$. Then we diagonalise the corresponding \mathbf{A} matrices using the program MATLAB and determine their eigenvalues and eigenvectors. In terms of the GGS-model considered here, these quantities are sufficient to allow to determine both the position dependent $\langle \delta Y_m(t) \rangle$, see Eq. (12), as well as the average of Eq. (12) with respect to m :

$$\langle \langle \delta Y(t) \rangle \rangle = \frac{1}{N} \sum_{m=1}^N \langle \delta Y_m(t) \rangle = \frac{F_0}{\sigma N \zeta} \sum_{i=2}^N \frac{1 - \exp(-\sigma \lambda_i t)}{\lambda_i}, \tag{13}$$

see Eq. (7).

As discussed in previous works, the intermediate time regime of Eq. (12) and (13), namely $1/\sigma \lambda_{\max} \leq t \leq 1/\sigma \lambda_{\min}$, (where λ_{\min} and λ_{\max} denote the minimal nonvanishing and the maximal eigenvalue of the set $\{\lambda_i\}$) is particularly revealing of the underlying GGS-topology.^{4,9,11,12,34,44,45} The same holds, of course, for $\langle Y_m(t) \rangle$ and $\langle \langle Y(t) \rangle \rangle$, see Eq (6) and Eq. (7). Thus linear chains display in the time-interval considered simple scaling with time,

$$\langle \langle Y(t) \rangle \rangle \sim t^\gamma \tag{14}$$

with $\gamma = 1/2$ for Rouse-type GGS;^{4,9,35} this behaviour is associated to anomalous diffusion and may be modelled through fractional differential expressions.^{8,11,12} On the other hand,

already the behaviour of star-molecules^{4,9} is more complex than Eq. (14); dendrimers, hyperbranched polymers and networks display intricate $\langle\langle Y(t) \rangle\rangle$ and $\langle\langle \delta Y(t) \rangle\rangle$ forms.^{9,44,45}

Our aim is now to focus on the dependence of the stretching $\langle \delta Y_m(t) \rangle$, Eq. (12) on m . As is evident from the inherent symmetry of the model this dependence reflects the distance of the bead on which the force acts from the ring backbone. We will also compare $\langle \delta Y_m(t) \rangle$ to its average over m , namely to $\langle\langle \delta Y(t) \rangle\rangle$, Eq. (13). The reason is that in several instances (for linear chains, for fractals and also in part for dendrimers and for small-world-network structures) Eq. (13) was found^{4,11,12,45} to be a qualitatively rather good description of the overall process. As will appear evident in the following, ring-combs show as a function of time a stretching which directly reflects the distance from the backbone of the bead on which the external force acts; in fact, this effect is so large that Eq. (13) ceases to be a qualitatively good description of the overall process. This fact has profound implications; it means that stretching is a much more revealing experimental method than macroscopic mechanical manipulations, which are related to Eqs. (10) and (11); we will return to this point in the next Section, after we present our evidence.

We start by presenting in Fig. 2 $\langle \delta Y_m(t) \rangle$, Eq. (12) for short times. For the plot we use dimensionless units, so that we set $\sigma \equiv 1$ and $F_0/\zeta \equiv 1$. Because of symmetry, we need only to focus on the distance of the m -th bead from the backbone. Thus $m = 1$ indicates that the bead considered belongs to the backbone and $m = 50$ means that the bead is at one of the tips of the chain-segments which constitute the comb. We depict first the situation at relatively short times, $0 \leq t \leq 1$, and display in Fig. 2 the parametric dependence of $\langle \delta Y_m(t) \rangle$ on m for $m = 1, 2, 49$, and 50 . Also given by a dashed line is the average $\langle\langle \delta Y(t) \rangle\rangle$.

We note from the start that for fixed t the quantity $\langle \delta Y_m(t) \rangle$ increases monotonically with m . This is simply understood on physical grounds, since acting farther away from the backbone extends a larger part of the linear-chain segment which constitutes the comb. Moreover, in the time interval considered in Fig. 2 there appear three types of behavior, namely those connected with the backbone ($m = 1$), with the tips ($m = 50$) and with the rest, given that the curves for points internal to the comb region (here $m = 2$ and $m = 49$)

coincide to a large degree. Clearly, the distinction between the three types of beads is their coordination number Z , which equals 3 for $m = 1$, 2 for $m \in \{2, 3, \dots, 49\}$, and 1 for $m = 50$. The physics of this stage is also clear: At short times each bead feels only its spring connections to its nearest-neighbors; a larger number of neighboring beads renders the extension under an equal force slower. Because of the large number, namely 48, of internal beads, the average $\langle \delta Y(t) \rangle$ follows closely the dynamics of the internal beads in the temporal range of Fig. 2.

Turning now to the behavior at very long times, we plot in Fig. 3 the situation for $M = 50$ and $0 \leq t \leq 10000$, where we display the curves corresponding to $m = 1, 2, 10, 20, 30, 40, 49$, and 50. As becomes evident by looking on the right side of the Figure, at long times the curves saturate. Here the above-mentioned monotonicity of the dependence of $\langle \delta Y_m(t) \rangle$ on m for fixed t is clearly evident. Evident, furthermore, is that the final extension of the object is (to a very good approximation) proportional to the value of m , *i.e.* practically proportional to its distance from the backbone. This proportionality, in fact, is getting more and more exact for increasing m . Note that such changes in the extension of the comb would lead to drastic changes in the electronic energy transfer between pairs of chromophores (one of which should be attached near to the backbone and the other close to the monomer which is pulled), given the strong dependence of the transfer rates on the mutual distance between the chromophores.

To render the dependence of the stretching on m more explicit, we plot in Fig. 4 $\langle \Delta_m(t) \rangle \equiv \{ \langle \delta Y_m(t) \rangle - \langle \delta Y_1(t) \rangle \} / (m - 1)$ for $m = 2, 10, 20, 30, 40, 49$ and 50. Here one can notice first the very good scaling of all the curves for t large, their spread getting to be less than 3%. The physical explanation of this finding relies on a quasistatic picture: At very long times the comb-ring diffuses as a whole through the solvent, its beads moving with practically the same velocity; at such long times the influence of the external force has propagated through the whole comb-ring, being counterbalanced at the level of each bead by the friction acting on it. Then the main contributions to $\langle \delta Y_m(t) \rangle$ are those stemming from the springs of the arms on which the force acts; in this way the situation is quite similar

to that encountered in the case of star-polymers:^{4,9} After its onset the force stretches one after another the springs of the arm on which it acts, a deformation which propagates until a bifurcation (or multifurcation) is reached, here the ring, in the case of a star-polymer the center. After reaching the bifurcation (or multifurcation) the force gets distributed vectorially along different paths and its influence on $\langle \delta Y_m(t) \rangle$ diminishes; from the point of view of the beads belonging to one arm, the rest of the polymer behaves as a very heavy, not-too-deformable mass. Hence in the stationary state mainly the springs between the backbone and the site on which the force acts contribute to $\langle \delta Y_m(t) \rangle$. Their stretching values are very close and they enter additively into $\langle \delta Y_m(t) \rangle$.

Returning now to Fig. 3 we notice that the $\langle \delta Y_m(t) \rangle$ show strong differences as a function of m ; we also note that the average $\langle \delta Y(t) \rangle$ is not a qualitative measure of the "typical" $\langle \delta Y_m(t) \rangle$ behavior anymore. From Fig. 3 for instance, we find that $\langle \delta Y(t) \rangle$ is close to $\langle \delta Y_m(t) \rangle$ only for m very close to $m = 25$. Thus situation differs here from previous findings for linear chains, and for dendrimers.^{4,9} The reasons for the differences found are complex: thus for linear chains and non-disperse samples (fixed N) the differences between the $\langle \delta Y_m(t) \rangle$ are rather limited (much less than an order of magnitude), while in the case of dendrimers the beads at the tips are extremely numerous and the behavior of $\langle \delta Y_m(t) \rangle$ due to them dominates the average $\langle \delta Y(t) \rangle$.

Already from Fig. 3 we can notice that the "approach to equilibrium", *i.e.* reaching the steady-state extension happens differently for different m . The situation is underscored by Fig. 4, where $\langle \Delta_m(t) \rangle$ highlights this effect: Thus the curve $\langle \Delta_2(t) \rangle$ raises quickest from 0 as t increases, a behavior followed then by $\langle \Delta_{10}(t) \rangle$. We see that while the curves for $m = 2$ and 10 reach 80% of the steady-state $\langle \Delta_m(t) \rangle$ for times around 200 and 1200 the curves whose m are larger than 10 reach their corresponding 80% values at later times. We interpret this as being again due to the underlying dynamical extension processes, which let the $\langle \delta Y_m(t) \rangle$ depend qualitatively on m . To analyze the intermediate region between short and long times more carefully, with the intention to uncover possible transient scaling behavior we plot in Fig. 5 $\langle \delta Y_m(t) \rangle$ *vs.* t in double logarithmic scales, focussing on the $10 \leq t \leq 1000$ regime.

Depicted are again the curves for $m = 1, 2, 10, 20, 30, 40, 49$, and 50 , as well as the averaged curve $\langle \delta Y(t) \rangle$. We remark at once that the average scales quite nicely, which allows to approximate it in this range by $\langle \delta Y(t) \rangle = ct^\gamma$, with $c = 0.57$ and $\gamma = 0.50$. The $\langle \delta Y_m(t) \rangle$ curves show slight deviations from scaling; however, where we to approximate their behavior in Fig. 5 by straight lines, we would assign them γ -parameters ranging from $g = 0.24$ for $m = 1$ to $\gamma = 0.53$ for $m = 50$. Without attributing excessive importance to these γ -values, we remark only that they allow to quantify the m -dependence of the stretching, $\langle \delta Y_m(t) \rangle$. Furthermore $\gamma = 0.5$ is the value obtained by stretching a macromolecular chain in the Rouse-domain;¹² deviations from this value are observable at very short times, where the motion of a single bead is ballistic, and hence $\gamma = 1$, and also at very short times, where we have saturation and hence $\gamma \simeq 0$. One can view the general situation as being mainly determined by the behavior of the chain-like segments; on top of it the curve for $m = 1$ mirrors the onset of the crossover to saturation, whereas that for $m = 50$ is more on the side of the short and medium times.

IV. CONCLUSIONS

In this article we have focussed on the stretching of ring-combs in external fields and have displayed, using the generalization by the Rouse-model to Gaussian structures³⁷ the dynamical unfolding of ring-combs when one of their beads is directly experiencing a pulling force. A physical realization would involve either having the corresponding bead charged, and the ring-comb being exposed to an external electrical field or, more in line with modern micro-manipulation techniques, acting on the bead through optical tweezers or by magnetic means. Distinct from situations involving linear-chains, fractals,^{10–13} or even dendrimers,^{4,9,43} comb-like macromolecules display a high sensitivity of their response to the distance from the backbone of the bead on which the external force acts. This precludes the theoretical use of quantities averaged over all beads in the description of the response; in mathematical terms, comb-like macromolecules require, besides the knowledge of the eigenvalues of the

connectivity matrix \mathbf{A} , also the knowledge of the corresponding eigenvectors. In descriptions that introduce other features (i.e. the hydrodynamic interactions, the excluded volume, the stiffness of the chains) the mathematical aspects are, in general, more complex; given our experience with dendrimers,^{4,9} however, we expect all the above qualitative statements (based on the Rouse model) to stay correct. One has to be well-aware of the fact that a quantitative comparison to experiments must take into account additional features.

We hasten to note that this has profound implications, given that such usually measured mechanical responses such as the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$, Eqs. (10) and (11), also involve the eigenvalues, but not the eigenvectors of \mathbf{A} . This is in line with $G'(\omega)$ and $G''(\omega)$ being macroscopically (and hence averaged) observable quantities. Comb-like structures, on the other hand, display new dynamical features, when probed by micromanipulation techniques. Thus, as shown in the previous Section, a quantity such as $\langle \delta Y_m(t) \rangle$ discloses a whole series of topological features in its temporal evolution: $\langle \delta Y_m(t) \rangle$ depends at short times mainly on Z , the functionality Z (number of connected beads) of site m ; at very long times $\langle \delta Y_m(t) \rangle$ reflects the distance of bead m from the ring backbone; furthermore, at intermediate times, $\langle \delta Y_m(t) \rangle$ may depend algebraically (as a power-law) on time, $\langle \delta Y_m(t) \rangle \sim t^\gamma$, where again γ is m -dependent. This intermediate regime may become even more rich as the size and the cross linking of the studied macromolecules increase. We hence view applying micromanipulation techniques on comb-molecules as a very worthwhile means of experimental study and suggest to combine them with fluorescence techniques; from the point of view of theory it may be valuable to extend our investigations to other macromolecular entities with complex topologies.

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Figure captions

Figure 1

Model of comb-ring with $M_1 = 9$ beads on the ring and with attached chains of $M_2 - 1 = 3$ beads each.

Figure 2

Plot of $\langle \delta Y_m(t) \rangle$, Eq. (12), as a function of time for several m values, $m = 1, 2, 49$, and 50 from below. Given through a dashed line is also the average $\langle \langle \delta Y(t) \rangle \rangle$, Eq. (13). The axes are in dimensionless units and we set $\sigma = 1$ and $F_0/\zeta = 1$, see text for details.

Figure 3

Same as Fig. 2, for $m = 1, 2, 10, 20, 30, 40, 49$, and 50 from below.

Figure 4

Plot of $\langle \Delta_m(t) \rangle \equiv \{ \langle \delta Y_m(t) \rangle - \langle \delta Y_1(t) \rangle \} / (m - 1)$ as a function of t , in order to display scaling at long times. The values of m are 2, 10, 20, 30, 40, 49, and 50. The two curves on the left side of the Figure belong to $m = 2$ and to $m = 10$, in this order, from above.

Figure 5

Plot of $\langle \delta Y_m(t) \rangle$ vs. t in double logarithmic scales; the m values are as in Fig. 3.